Measurements and model calculations of HNO₄: Implications for HO_x

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Establishing a quantitative understanding of the abundance of peroxynitric acid (HNO₄) is of interest because the reaction of OH with HNO₄ is believed to be a significant sink for HO_x in the lower stratosphere and upper troposphere. We present concentration profiles of HNO₄ obtained by the MkIV Fourier transform infrared spectrometer using the solar occultation technique during two flights, one at 35°N on 25 September 1993 (930925) and the other near 66°N on 7 May 1997 (970507). The observations of HNO₄ present an apparent dilemma: the calculated profile for HNO₄ found using standard kinetics is in relatively good agreement with the mid-latitude observations, but the calculated profile for HNO₄ found using the same kinetics overestimates the high-latitude summer observations by nearly a factor of two. Resolution of this dilemma is the focus of our investigation. We show that introduction into our photochemical model of a speculative long-wave ($\lambda > 650$ nm) photolytic pathway for HNO₄ leads to good agreement between theory and observation of HNO₄ for both the mid-latitude and high-latitude regions. Implications for the budget of HO_x are also discussed.